PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements relating to Nitrocellulose

We, E. I. Du Pont De Nemours and Company, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of treating nitrocellulose to render it safer for transport and storage.

Nitrocellulose is a cellulose derivative which has found extensive use in a wide variety of industries. It is prepared commercially by the direct nitration of cellulose in any convenient form, such as purified woodpulp or cotton linters. The nitration is usually performed with an acid mix consisting essentially of nitric acid, sulphuric acid, and water in suitable proportions, although other nitrating media are sometimes used.

Nitrocellulose is rarely, if ever, transported or stored in a dry form because of its high sensitivity to ignition when dry, but is almost always maintained in a wet form. Where the presence of moisture can be tolerated in the end use, the nitrocellulose is wetted with water. Commercial water-wet nitrocellulose characteristically contains about 20—25% water. For some end uses, however, the presence of moisture in nitrocellulose is extremely objectionable and in such cases the nitrocellulose is wetted with an alcohol, usually ethanol, isopropanol, or butanol. Commercial alcohol-wet nitrocellulose normally contains about 30 to 35% total volatiles, the latter being primarily an alcohol with small amounts of moisture. Throughout this specification, the term "wet nitrocellulose" is intended to designate nitrocellulose which has been wetted with water, an alcohol, or another suitable liquid.

The density of nitrocellulose which has not been compressed or compacted in any way is in the neighbourhood of about 10 lb./cu.ft.(dry basis). For storage and transport this material is rammed into cylindrical drums to a density of 20—25 lb./cu.ft. The commercial nitrocellulose drum contains on the average of about 135—160 lb. of nitrocellulose (dry basis) per drum.

Though wetting the nitrocellulose, as described above, clearly minimises the hazards of storing and transporting it, some danger still remains. For example, if an open standard commercial drum of alcohol-wet nitrocellulose should ignite, a violent eruption will ensue which will send a ball of fire upwards for a distance of 25 to 50 feet and may propel a shower of burning particles and sparks a considerable distance laterally outward from the drum. In the event of accidental ignition, any persons in the immediate vicinity are likely to be seriously injured. In addition, the great shower of burning particles and sparks represents an extreme hazard in that other drums of nitrocellulose or other inflammable material in the area may also be ignited, leading to an even more widespread and dangerous conflagration.

It is an object of the present invention to treat nitrocellulose in such a way as to reduce greatly the effect of accidental ignition.

According to the invention wet fibrous nitrocellulose is subjected to a compressive force of a minimum magnitude given by $P = 2M + 6400$ wherein P is the pressure in pounds per square inch and M is the median fibre length in microns of the nitrocellulose. The resulting compressed product, which is in the form of a compact sheet or irregularly shaped flat particles, may then be broken down into smaller particles by a mild granulating action if necessary. The compression may be performed in any suitable way, and the particular apparatus which is used forms no part of the invention.

The fibre length distribution of fibres may be readily determined in an accurate manner, for example by means of a four-screen Clark

Classifier, manufactured by the Thwing-Albert Instrument Co. This latter instrument is widely used and relied on in the paper and pulp industry. (See Reed, A. E. and Clark, J. d'A, "An Instrument for Rapid Fractionation of Pulp", TAPPI (published by the Technical Association of the Paper and Pulp Industry), Vol. 33, No. 6).

It is vital that the pressure applied be not less than the amount determined by the above relationship, if the effect of accidental ignition is to be substantially reduced. Lower pressures, though sometimes effecting a slight improvement in some of the properties of a nitrocellulose, will not increase its safety characteristics. Generally speaking, any pressure greater than that indicated above as the minimum requirement is suitable. It has been found, however, that pressures in the vicinity of 15,000 psi. or higher, which is substantially above the minimum required, yield consistently fine results inasmuch as such pressures consistently serve to convert the conventional fibrous nitrocellulose into a compact, dense, completely free-flowing product presenting a greatly reduced fire risk. For most industrial nitrocellulose products, therefore, it is preferred to operate in the range of 15,000 to 17,000 psi. though lower pressures above the minimum defined above are definitely effective. The only upper limitation on the amount of pressure which may be employed is the pressure at which the nitrocellulose feed begins to char. As a practical matter, however, economic considerations dictate that pressures above the preferred 15,000 to 17,000 psi. range would rarely be used, since they offer no particular advantages.

The pressure may be applied to the nitrocellulose in any suitable manner, as for example by a pair of co-operating rollers. For example, the wet fibrous nitrocellulose may be placed on a simple roll mill of the type which is conventional in the rubber industry for compounding rubber stocks prior to curing. Such a roll mill characteristically consists of a pair of co-operating rollers spaced a short distance apart or even initially in contact and driven in opposite directions. One roller may be driven in a clockwise direction at a given speed, and the other may be driven in a counter-clockwise direction at the same or a different speed, or the second roller may idle. The space between the rollers is not generally critical, and may be varied widely, the preferred setting in any instance depending on the type of nitrocellulose, the rate of nitrocellulose feed, and various other factors. Similarly, the thickness of the nitrocellulose disk-like particles or sheet formed by the rollers may vary from exceedingly thin films a few thousandths of an inch thick to relatively thick particles or sheets.

After the wet nitrocellulose has been compressed, as described above, it may be crumbled by subjecting it to a mild granulating action. The latter term is used in its broadest sense to include any mechanical working or agitation which tends to break up the flat particles or sheets into a smaller particulate form. In many cases the mere dropping of the particles or sheets from the rollers to the surface on which the rollers are mounted is sufficient to crumble all or a significant proportion of the compressed nitrocellulose. Depending upon the thickness of the sheets or particles and the type of nitrocellulose, it may be desirable to subject them to a mild tumbling or agitation or to the action of slowly rotating teeth to ensure that the pressed nitrocellulose is reduced to a particulate form for packing into a drum. For this purpose any mild mechanical working is effective, including for example, shaking, crumbling, pulverizing, vibrating, chewing, comminuting and tumbling. In many cases, however, the flat disk-like particles which result from the compression are only a few inches wide on the average and may themselves be loaded into a drum without first breaking them up into still smaller particles.

The invention is illustrated in the accompanying drawing, in which the Figure represents an elevational schematic view of one form of apparatus suitable for carrying out the process of the invention.

Referring now to the drawing, (1) and (2) represent a pair of abutting rollers, roller (1) idling on its shaft and roller (2) being driven in the direction indicated by any suitable drive means (not shown). Roller (2) is journalled in the ends of a pair of hydraulic ram arms (3) by means of which it may be forced to bear against roller (1) under great pressure. Beneath the rollers (1), (2) is a shredder or comminuter (5) containing two sets of parallel, rotating, intermeshing teeth (6), (7).

The wet nitrocellulose from a hopper (4) above the rollers feeds into the roller set (1), (2) and is there severely compressed into a hard, dense, compact, non-fibrous, sheet-like form, which, in turn, falls through the comminuter (5), where the compressed material is broken up, the resulting particles falling for collection, for example, onto a conveyor (8).

Other suitable means for compressing the wet nitrocellulose into compact sheets or into flat, disk-like particles may be used. For example, intermittent ramming may be used, or a single heavy roller on a flat surface. It will be readily apparent, however, that the continuous action of a roll mill offers attractive economic advantages over other suitable methods, though the invention is by no means limited to this particular type of apparatus.

The process of the invention is primarily applicable to the treatment of so-called "industrial nitrocellulose", i.e. conventional fibrous nitrocellulose products having a nitrogen content of 10.8% to 12.3% and used industrially for making, for example, lacquers, coatings and plastics, as distinct from gun-

cotton and other nitrocellulose propellant products having a higher nitrogen content. The latter varieties of nitrocellulose, having a nitrogen content greater than 12.3%, are usually referred to in the trade as "military grade" or "powder grade" nitrocellulose. Though the invention may have some beneficial effects in connection with military grade nitrocellulose, the greatest benefits are derived in the industrial nitrocellulose field and this represents by far the most significant and preferred application of this invention.

The invention is further illustrated by the following Examples.

EXAMPLE I

200 lb. per hour of alcohol-wet nitrocellulose (12%N_2) containing 19% isopropyl alcohol and having a median fibre length of 650 microns were fed continuously to a pair of co-operating metal rollers 6 inches in diameter and 12 inches in length. One of the rollers was rotated in a clockwise direction at about 20 rpm and the other roller was rotated in a counter-clockwise direction at about 28 rpm. The peripheries of the rollers were spaced about 0.015 inches apart. The force applied to the rollers was such that the pressure on the nitrocellulose in the nip was about 17,000 psi. The compressed wet nitrocellulose disk-like sections which emerged from the rollers were permitted to fall 8 inches to the floorpan beneath the rollers where a substantial proportion of them crumbled by the impact of the fall.

EXAMPLE II

Approximately 3000 lb. per hour of alcohol-wet 5—6 second regular soluble nitrocellulose (12%N_2) containing 21% ethyl alcohol and having a median fibre length of about 2000 microns, were fed continuously to a pair of co-operating metal rolls 15 inches in diameter and 39 inches in length. One of the rolls was rotated in a clockwise direction at about 20 rpm and the other was rotated in a counter-clockwise direction at approximately 20 rpm. A total pressure of about 50 tons was applied by means of hydraulic cylinders bearing upon both ends of one roll; the second roll being fixed. This total pressure was equivalent to a pressure on the nitrocellulose of about 16,500 psi. The dense, compact, compressed wet nitrocellulose disk-like sections which emerged from the rolls were permitted to fall 10 inches into a cutting device, comprised of a horizontal rotating shaft (150 rpm) and a stationary shaft, each fitted with a series of intermeshing **T**-shaped blades. The final products consisted of flakes averaging about 1 to 2 in.^{2} in area and 0.040 inch. The free-flowing product was readily packed into an ICC-6J galvanised steel drum (inner diameter $22\frac{1}{2}$ inches, inner height $33\frac{1}{4}$ inches) at 200 lb. dry nitrocellulose and alcohol added to give a final alcohol content of 25%.

EXAMPLE III

Approximately 3000 lb. per hour of water-wet nitrocellulose (11.6%N_2), containing 23% water and having a median fibre length of about 650 microns, were fed continuously to the pair of co-operating metal rollers utilised in Example I. The roller speeds and loading pressure, as well as the method of disintegrating the disk-like sections produced, were identical with those specified in Example I. The final water-wet, dense nitrocellulose product consisted of flakes averaging about 1 to 2 in.^{2} in area and 0.040 in. thick. The free-flowing product was readily packed into a standard ICC-6J galvanised steel drum at 200 lb. dry nitrocellulose and water added to give a final water content of 23%.

EXAMPLE IV

Approximately 3000 lb. per hour of alcohol-wet, one half second regular soluble nitrocellulose (12% N_2), containing 21% ethyl alcohol and having a median fibre length of about 650 microns, were fed continuously to the pair of co-operating metal rollers utilised in Example I. The roller speeds and loading pressure, as well as the method of disintegrating the disk-like sections, were identical with those specified in Example I. The final alcohol-wet, dense nitrocellulose product consisted of flakes averaging about 1 to 2 in.^{2} in area and 0.040 in. thick. The free-flowing product was readily packed into a standard ICC-6J galvanised steel drum at 240 lb. dry nitrocellulose and alcohol added to give a final alcohol content of 25%.

The tests which have been performed indicate quite conclusively that nitrocellulose which has been treated in accordance with the present invention is much safer to ship and to store than is the conventional fibrous nitrocellulose currently available from commercial sources, as is illustrated by the following Examples.

EXAMPLE V

An ICC-6J galvanised steel drum was filled to the 50% level with ordinary commercial, isopropanol-wet, fibrous nitrocellulose (12% N_2, 30% total volatiles). A second identical drum was filled to the 50% level with the treated nitrocellulose material of Example I adjusted to a 30% total volatiles content. Both drums were ignited simultaneously with separate squibs. The results of both ignitions are indicated by the following table:

Time after ignition (min.)	*Regular untreated material*	*Treated material of Example I*
1/12	start eruption	mild flame
1/4	end eruption	mild flame
1	mild flame	mild flame
2	mild flame	mild flame
3	mild flame	mild flame
4	mild flame	mild flame
6	mild flame	mild flame
8	mild flame	mild flame
10 (flame extinguished with water from fire-hose)	a little nitrocellulose left in bottom	half of the original nitrocellulose unconsumed

EXAMPLE VI

The procedure of Example V was repeated with both the regular and treated nitrocellulose adjusted to a 25% total volatiles content. The results of both ignitions are recorded in the following Table:

Time after ignition (min.)	*Regular untreated material*	*Treated material of Example I*
1/12	mild flame	mild flame
1/4	mild flame	mild flame
1	mild flame	mild flame
2	eruption	mild flame
3	mild flame	mild flame
4	mild flame	mild flame
6	mild flame	small flare-up
8	mild flame	small flare-up
10	mild flame	small flare-up
12 (flame extinguished with water from fire-hose)	no nitrocellulose left	a little nitrocellulose left in bottom

EXAMPLE VII

The procedure of Example V was repeated with the treated nitrocellulose adjusted to a 20% total volatiles content. The results of both ignitions are recorded in the following Table:

Time after ignition (min.)	*Regular untreated material*	*Treated material of Example I*
1/12	mild flame	mild flame
1/4	start eruption	mild flame
1	end eruption	mild flame
2	mild flame	small flare-up
3 (flame extinguished with water from fire-hose)	a little nitrocellulose left in bottom	$\frac{3}{4}$ of the original nitrocellulose unconsumed

In Examples V—VII, the term "mild flame" refers to a low quiet flame extending no more than about 1—2 feet into the air above the top surface of the nitrocellulose. By "small flare-up" is meant a modest flame of some vigour extending 5—10 feet in the air. The term "eruption" designates a vigorous and extremely active flame shooting upwards a distance of 25-50 feet in the air and propelling a shower of burning particles and sparks laterally outward for a distance of 24—40 feet.

It will be readily apparent from the foregoing that in the event of an accidental or spontaneous ignition, drums containing the treated nitrocellulose are considerably safer than drums containing ordinary commercial material. Upon ignition, the latter burns with a vigour and intensity which in most instances are many times greater than those of the treated material. A further factor of equal importance is that the regular material flares up much more quickly than does the treated material. On ignition, the regular material erupts almost instaneously giving little or no time for men in the area to escape or take steps to extinguish the flame. The treated material, on the other hand, either does not erupt at all or flares up only after a time lag sufficiently long to permit men to stand clear or to extinguish the blaze.

Numerous advantages accrue from the above-described burning properties of nitrocellulose treated in accordance with the present invention. The treated material is, of course, much safer in the event of ignition with respect to personnel and property in the vicinity since the blaze is much less severe and more easily extinguished if it should occur. In view of these improved safety characteristics, it may often be possible to reduce safely the total volatiles content, e.g., alcohol with which the nitrocellulose is wetted, thereby effecting a substantial saving in the alcohol and in freight costs.

In addition to the safety and attendant advantages which are achieved by means of the present invention, several other incidental but extremely important advantages also result. For one thing, the bulk density of the treated material is much higher than that of the ordinary material. It is thus possible to pack the customary contents of a commercial nitrocellulose drum (about 230 lb. of material) in a container which is 25—30% smaller in volume. On the other hand, if the container is not reduced in size, it is now possible to pack the container with more nitrocellulose than has heretofore been possible. From the standpoint of economy in shipment and storage, this is obviously an extremely valuable achievement. The following Table illustrates the differences in bulk densities between several types of regular commercially available nitrocellulose products before and after they have been treated in accordance with the process of the present invention:

			Bulk Density (Dry Basis)	
Nitrogen, %	*Wetting Agent*	*Total Volatiles, %*	*Regular Product (lb./cu.ft.)*	*Treated Product (lb./cu.ft.)*
12.0	Isopropanol	19	9.1	16.6
12.0	Isopropanol	20	14.2	24.0
12.0	Isopropanol	21	6.6	12.1
11.6	Water	23	9.8	14.0

In addition to a marked increase in the bulk density of the nitrocellulose, the process of the present invention also enhances the ability of the nitrocellulose product to enter into solution, as is indicated by the following Example.

EXAMPLE VIII

A portion of a regular commercial nitrocellulose product containing 11.6% nitrogen was wetted with ethanol and set aside. A similar portion of the same nitrocellulose, similarly wetted, was treated in accordance with the technique described in Example I above. A sample of each material containing 251 g. of nitrocellulose (dry basis), was placed in a separate 2-litre beaker containing 451 g. ethanol. The contents of each beaker were agitated for 30 seconds with a single-paddle stirrer one inch from the bottom operating at 300 rpm. 989 g. of toluene were then added to each beaker and the contents of the beakers were then agitated for an additional 30 seconds with the stirrer. Thereafter, 359 g. of 88% ethyl acetate was added to each beaker and the agitator was turned on again. The agitator was permitted to run continuously, except that it was stopped every 15 minutes to check the degree of solution, until the nitrocellulose was completely dissolved. On this basis, the regular commercial material was found to completely dissolve in $2\frac{1}{2}$ hours whereas the material which had been treated in accordance with the process of the present invention dissolved in $1\frac{1}{2}$ hours.

In addition to all of the foregoing advantages, nitrocellulose which has been treated in accordance with the present invention has the still further advantage of remaining free-flowable at all times even when stored in drums for extended periods. Regular commercial material when placed in a container invariably forms a matted mass known as "hard-pack", and the resistance of this hard-pack to flow has plagued users of nitrocellulose for many years. In order to empty a commercial container of ordinary wet nitrocellulose, it is necessary for the operator to tilt the container and to extract the material manually with a pitchfork or similar implement or to use some other mechanical aid to break the hard-pack and dislodge the nitrocellulose so that it will flow from the container. This is an inconvenient and money-wasting operation from the point of view of most industrial users of nitrocellulose, and is completely eliminated by the present invention. Nitrocellulose which has been treated in accordance with the present process will not form hard-pack and will flow freely and quickly from any container in which it has been stored, even for long periods.

Throughout the specification, the pressures to which the fibrous nitrocellulose is subjected are always referred to in terms of pounds per square inch. It must be borne in mind that the precise pressures pertinent in any case may vary slightly from those figures mentioned depending on the size, efficiency, and surface conditions of the particularly rollers or other equipment utilised to practice the invention. To some extent, even the age of the equipment will affect the pressure employed. For example, the spacing between the rollers shown in the drawing on one occasion was nil prior to the start of the nitrocellulose feed, but after the rollers had been in operation for some time a spacing of about 0.040 inch was noted when the feed was stopped, as a result of flexing of the rollers and compression in the hydraulic loading system. These individual equipment characteristics will, therefore, affect slightly the actual pressures required in any single instance, but the differences from the figures mentioned will never be very great, i.e. not more than a few per cent at most from case to case.

The shape or dimensions of the compressed nitrocellulose sections which result from the compression step is not critical to the invention. The nitrocellulose may be pressed into the form of relatively long continuous sheets or it may be pressed into numerous relatively small, individual, flat, irregularly-shaped, disk-like particles a few inches across. The latter are more likely to result if a roll mill is used and have the advantage that they require a minimum, if any, of subsequent mechanical working to break up the compressed nitrocellulose.

WHAT WE CLAIM IS:—

1. Process for the treatment of fibrous nitrocellulose to render it safer for transport and storage, which comprises subjecting the fibrous nitrocellulose while wet to a compressive force of minimum magnitude given by $P = 2M + 6400$, where P is the pressure in pounds per square inch and M is the median fibre length in microns of the nitrocellulose.

2. Process according to claim 1, wherein the resulting sheet or flat particles of nitrocellulose are subsequently broken down into smaller particles by a mild granulating action.

3. Process according to claim 1 or 2, wherein the pressure is applied to the fibrous nitrocellulose by means of a pair of initially contacting or closely spaced rollers rotating in opposite directions.

4. Process according to any of the preceding claims, wherein the fibrous nitrocellulose is wet with water.

5. Process according to any of claims 1 to 3, wherein the fibrous nitrocellulose is wet with an alcohol.

6. Process according to any of the preceding claims, wherein the fibrous nitrocellulose has a nitrogen content of 10.8—12.3%.

7. Process according to any of the preceding claims, wherein the fibrous nitrocellulose is subjected to a compressive force of 15000—17000 pounds per square inch.

8. Process for the treatment of fibrous nitrocellulose according to claim 1 substantially as described by reference to the accompanying drawing.

9. Process for the treatment of fibrous nitrocellulose according to claim 1 substantially as described in Examples I—IV.

10. Nitrocellulose which has been rendered safer to transport or store by a process claimed in any of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
9 Staple Inn, London, W.C.1.

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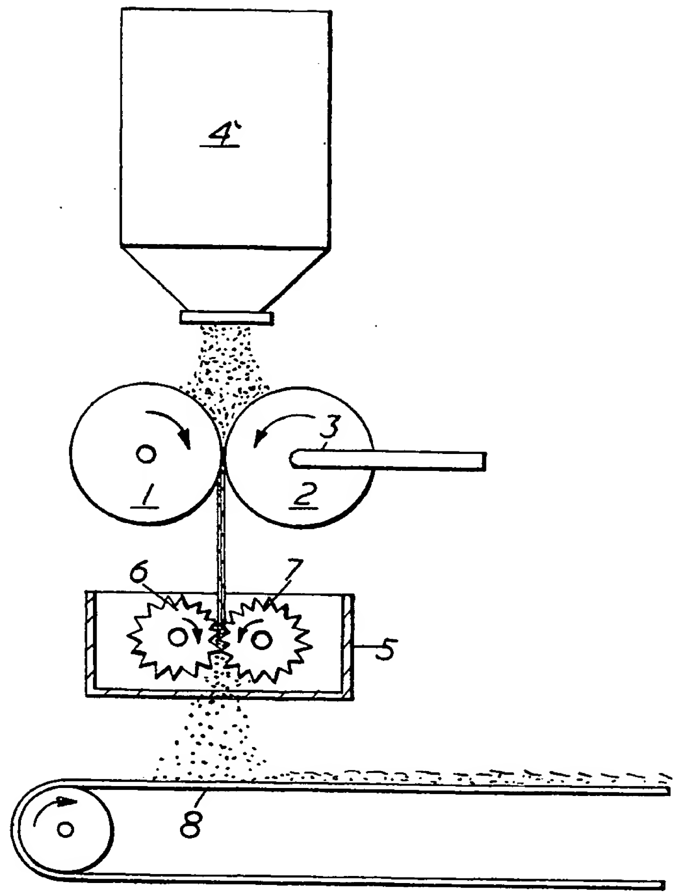
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